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DATA COMPILATION ON VANADIUM OXIDES

M. NEUBERGER

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The change in crystal structure at the transition temperature in several of the vanadium oxides, causes a drastic change in resistivity as the material is heated (or cooled). This phenomenon is being applied to the manufacture of a number of devices.

All available information on the crystal structure, physical, mechanical, thermal, optical, magnetic and electronic properties of bulk and film samples, has been tabulated in this compilation. Graphs illustrating these features are included.

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Thermal Properties						
Mechanical Properties						
Crystallographic Properties						
Phase Diagrams						
Electronic Switching Devices						

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ABSTRACT

The change in crystal structure at the transition temperature in several of the vanadium oxides, causes a drastic change in resistivity as the material is heated (or cooled). This phenomenon is being applied to the manufacture of a number of devices.

All available information on the crystal structure, physical, mechanical, thermal, optical, magnetic and electronic properties of bulk and film samples, has been tabulated in this compilation. Graphs illustrating these features are included.

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INTRODUCTION

Several vanadium oxides, $VO_{0.8-1.3}$, V_2O_3 and an entire series of non-stoichiometric vanadium oxides, show a crystallographic transformation from a low to high temperature phase. According to Hyland,* there is no extensive rearrangement of the atoms, only slight distortions of the original atomic grouping which is rapidly reversible at the transition temperature. Fillingham in an optical study of the domain structure in VO_2, indicates that displacement of the atom positions is small and comprises only slight distortions of the VO_6-octahedra chains as vanadium atom doublets form, alternately nearer to and farther from one another in the low temperature (monoclinic) phase. As the crystal moves through the transition temperature, domain patterns show only in the monoclinic phase, there are no domains evident in the tetragonal phase.

These alternating long and short separations of the cations along the a-axis (2.65Å and 3.12Å) shift above the transition temperature and the cations form a body-centered tetragonal array; V-V = 2.87Å along the c-axis. As a result, $a_{monoclinic} = 2c_{tetragonal}$ and Z-2 becomes Z-4.

This shift in crystal structure must evidently exercise a strong effect on the electronic properties of the several vanadium oxides and, consequently, on the band structure. The most marked and useful change is a rise in conductivity as the vanadium dioxide is heated through its transition temperature of 68°C where the material passes from a semiconducting to a metallic state. The conductivity is 5 orders of magnitude in VO_2 and 9 orders of magnitude in V_2O_3. The shift is also anisotropic and, depending on the sample quality, may also exhibit hysteresis.

Single crystals in the series V_nO_{2n-x} with x equal to an integer, have been studied by Okinaka et al., Kosuge and Nagasawa. Transition temperatures in this series vary from 68°C to -140°C. The composition V_5O_9 has a resistivity jump on cooling through 125°K of $\sim 10^7$ Ωcm and together with V_6O_{11} shows an increase in thermal emf at the transition temperature from -10 to -800 μV/°K.

* All references are listed alphabetically by name, in the bibliography at the end of this report.

This change in the several properties of the vanadium oxides is being applied to the manufacture of a variety of switching and modulation devices, since the time constant is about 20 nanoseconds. (Schmidt, Cope & Penn, Walden, Kennedy & Collins, Van Steensel).

Other electronic and physical properties also show a discontinuity at the transition temperature; magnetic susceptibility, thermoelectric power, specific heat, thermal expansion, reflectivity and transmission spectra. Graphs illustrating these features are included.

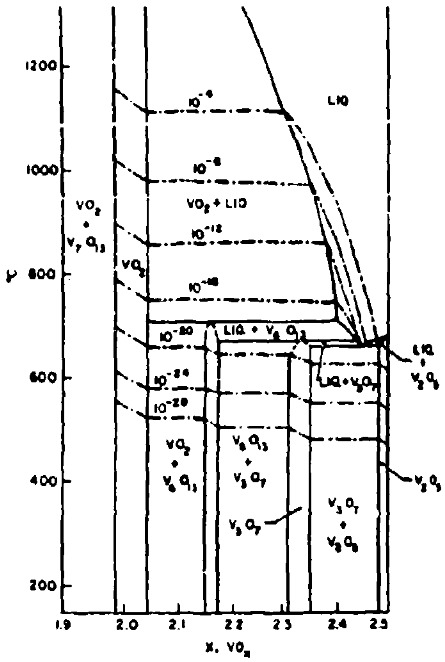
Band structures have been formulated, based in general on the theoretical considerations of Goodenough, by many experimentalists. These include Hyland, Verleur et al., Bongers, Powell et al., Berglund & Guggenheim, Austin & Turner, Mokerov & Rakov and Adler. Austin & Mott, in a recent discussion of the transition metal oxides, ascribe their properties to Coulomb interactions between the d-electrons and a strong electron-lattice coupling. With others in this field, they also agree that disorder and defects have a marked influence in leading to localized electron states. There is, apparently, a general agreement that the transition phenomena are primarily lattice dominated, but a band structure which will satisfy both electrical and optical considerations has not yet been formulated.

In general, electrical and magnetic data yield a one-electron band model with relatively large electron-phonon interactions. In a band structure derived from optical data, Verleur et al. propose a model for VO_2 above the transition temperature, in which filled valence bands (associated with the oxygen) are separated from partially filled conduction bands (arising from the vanadium), with the lowest vanadium bands slightly overlapping one or more of the partially filled bands. On this basis, the VO_2 at temperatures above the transition, would be a semi-metal, rather than a metal. In the model derived from optical data, VO_2 at temperatures below the transition would have electrons trapped in localized levels or occupying two completely filled bands. In any event, much more experimental data on crystals of high purity and stoichiometric quality are needed to choose a realistic band structure model.

Repeated cycling of crystals of VO_2 causes cracking and to obviate this difficulty, Hensler, Fuls, Rozgony and their associates have prepared sputtered, polycrystalline films, 500 to 4000 Å thick, annealed at 400°C. These randomly oriented thin films, when carried through the heating and cooling cycle, show new random configurations with the same properties as previously and may, therefore be considered stable.

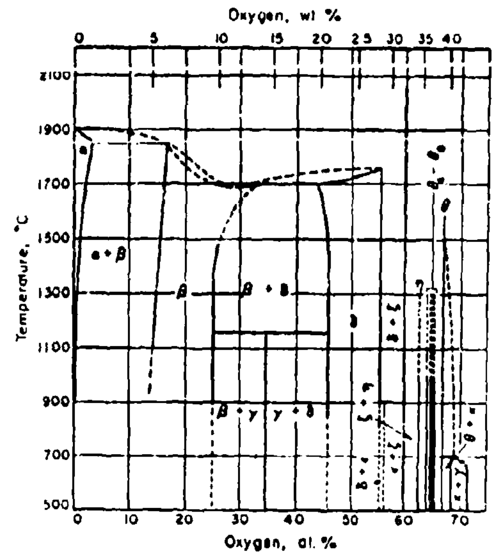
Vanadium monoxide is stable over a composition range of $VO_{0.8}$ to $VO_{1.3}$. Density measurements indicate that stoichiometric samples are highly defective and analysis of infrared spectra by Ariya & Golomolzina led them to the conclusion that the monoxide comprises regions of vanadium alternating with regions of V_2O_3.

The data tables which follow, cover all vanadium oxides known to date, including those which do not show any phase transition. Pertinent curves for the several properties covered in the tables are inserted, following each stoichiometric compound. A few graphs have been included for chromium, aluminum or titanium doped vanadium oxides for their value in device applications, but these materials will be more fully covered in a later report.



Vanadium-Oxygen phase diagram, on the basis of recent data.
- - - - - - oxygen partial pressure (atm)
—·—·— estimated oxygen pressure

MacChesney & Guggenheim,
Kosuge, B
MacChesney et al.



Vanadium-Oxygen System

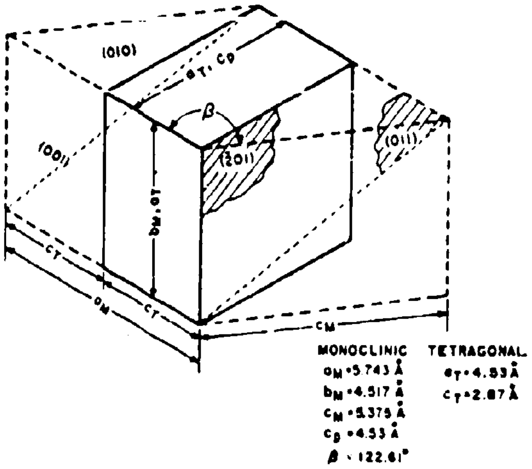
Stringer

Phase Analyses of vanadium oxides by magnetic susceptibility measurements and x-ray diffraction measurements.

Kosuge, B

VO_x	Phase	VO_x	Phase	VO_x	Phase
1·50	V_2O_3	1·84	$V_6O_{11}+V_7O_{13}$	2·30	$V_6O_{13}+V_3O_7$
1·51	V_2O_3	1·85	$V_6O_{11}+V_7O_{13}$	2·32	V_3O_7
1·52	$V_2O_3+V_3O_5$	1·86	V_7O_{13}	2·34	V_3O_7
1·64	$V_3O_5+V_2O_3$	1·87	$V_7O_{13}+VO_2$	2·36	$V_3O_7+V_2O_5$
1·65	V_3O_5	1·97	$VO_2+V_7O_{13}$	2·38	$V_3O_7+V_2O_5$
1·66	V_3O_5	1·98	$VO_2+V_7O_{13}$	2·40	$V_3O_7+V_2O_5$
1·67	V_3O_5	1·99	VO_2	2·42	$V_3O_7+V_2O_5$
1·68	$V_3O_5+V_4O_7$	2·00	VO_2	2·45	$V_2O_5+V_3O_7$
1·73	$V_4O_7+V_3O_5$	2·01	VO_2	2·47	$V_2O_5+V_3O_7$
1·74	V_4O_7	2·02	VO_2	2·48	V_2O_5
1·75	V_4O_7	2·03	$VO_2+V_6O_{13}$	2·50	V_2O_5
1·76	$V_4O_7+V_5O_9$	2·10	$VO_2+V_6O_{13}$		
1·77	$V_5O_9+V_4O_7$	2·15	$V_6O_{13}+VO_2$		
1·78	$V_5O_9+V_4O_7$	2·16	V_6O_{13}		
1·79	$V_5O_9+V_4O_7$	2·166	V_6O_{13}		
1·80	V_5O_9	2·17	V_6O_{13}		
1·81	$V_5O_9+V_6O_{11}$	2·18	$V_6O_{13}+V_3O_7$		
1·82	$V_6O_{11}+V_5O_9$	2·20	$V_6O_{13}+V_3O_7$		
1·83	V_6O_{11}	2·25	$V_6O_{13}+V_3O_7$		

CRYSTAL STRUCTURE

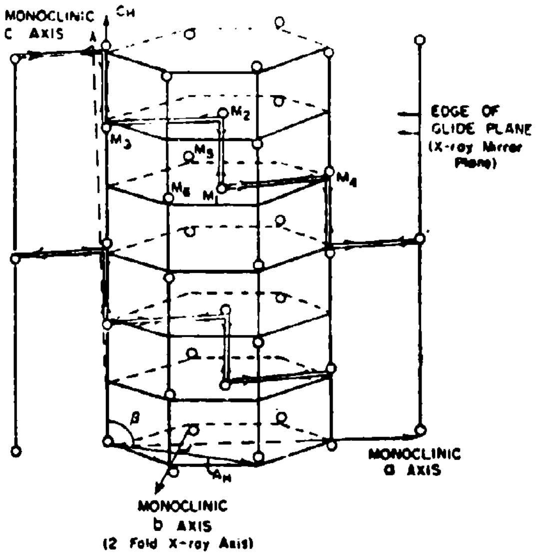


VO_2

Relation between tetragonal unit (high temperature, solid lines) and monoclinic unit (low temperature, dashed lines).

Major monoclinic planes are shown.

Simplified structure of V_2O_3 showing only the vanadium ion position.



THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP.(°K)	REFERENCES
Formula		VO				
Stability range		$VO_{0.8}$-$VO_{1.3}$		(Possible: VO= $V+V_2O_3$)		Stringer, Adler
Molecular Wgt.		66.95				
Density		5.92	g/cm^3	6.49 (calc.)		Donnay
Color		light grey				Handbook
Symmetry		cubic				Donnay
Space Group		Fm3m Z-4				Donnay
Lattice Parameters	a_o	4.099	Å			Massard et al.
		4.093				Donnay
	V-V	2.93				Bongers

VO_x	a_o(Å)	Density (g/cc)	Vacancies (%)		
0.86	4.034	5.736	37.0	sintered at 1300°C	Banus et al.
0.96	4.058	5.674	31.7		
0.99	4.068	5.602	30.8		
1.02	4.077	5.583	28.9		
1.23	4.133	5.329	21.2		
1.30	4.14	5.85	22	single crystal, zero oxygen vacancies	

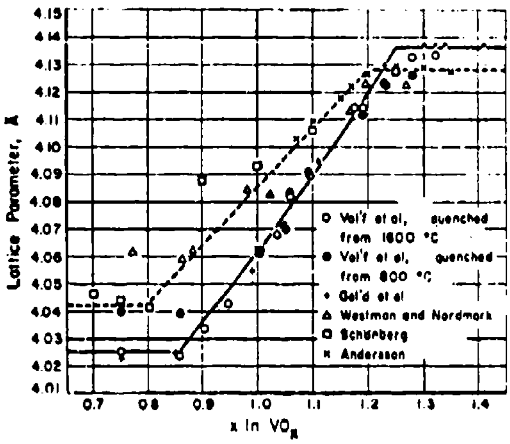
PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP.(°K)	REFERENCES
Melting Point		1720	°C	in vacuo		Stringer
Specific Heat		0.014	cal/g °K		50	TPRC, p. 528
		0.158			300	
		0.225			1700	

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Resistivity	$VO_{.83-.86}$	$VO_{1.02}$	$VO_{1.2}$			
	8×10^{-4}	6×10^{-3}	Ω-cm	sintered	4	Honig et al.
	8×10^{-4}	5×10^{-3}	9×10^{-1}	sintered, shows no T_c	77	Banus et al.
	8×10^{-4}	2×10^{-3}	10^{-2}		300	
	$VO_{.919}$	$VO_{1.147}$	$VO_{1.25}$			
	2×10^{-3}	3×10^{-2}	— Ω-cm	sintered to 90% density, shows no T_c	100	Kawano et al.[A]
	10^{-3}	2×10^{-2}	2×10^{-1}		115	
	8×10^{-4}	5×10^{-3}	6×10^{-3}		300	
		2×10^{-3}	Ω-cm	1-5μ, epitaxial film on MgO, no T_c	77-300	Takei & Koide[A]
		0.4×10^{-3}		0.3μ film, $VO_{0.2}$	300	Hensler et al.
		0.8×10^{-3}		0.1μ film, $VO_{1.2}$		
Temp. Coeff.		-3×10^{-5}	$°C^{-1}$	0.3μ film, $VO_{0.2}$		Hensler et al.
		$- 10^{-3}$		0.1μ film, $VO_{1.2}$		
Resistivity		10^{7}	Ω-cm	$VO_{0.9}$	94	Austin
		10^{6}		VO, single crystal	83	Morin
		10^{-2}			300	
Transition Temp.	T_c	114 126	°K	cooling heating		Morin
Pressure Coeff.	dT_c/dP	-3	10^{3} °K/bar	P= 25 kbars	94, 113	Austin
Transition Temp.		88-125	°K	NMR meas., range due to variations in stoichiometry		Warren et al.

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Energy Gap		6	meV	high V content		Banus et al.,
		0.157	eV	low V content		Kawano et al. [A]
Seebeck Coeff.	$VO_{.88}$	$VO_{.99}$ $VO_{1.05}$ $VO_{1.23}$				
	-12	-4 +5 +22	μV/°K	sintered	300	Banus et al.
	$VO_{.85}$	VO $VO_{1.05}$ $VO_{1.26}$				
	-5	+3 +8 +26		sintered to	300	Kawano et al. [B]
		0 +3 +17		90% density		
Magnetic Susceptibility	χ_g	6	10^{-6} cgs	sintered, VO	300	Massard et al.
		8		sintered	90	Bogdanova & Loginov
		5			300	
	$VO_{.92}$	$VO_{1.07}$ $VO_{1.26}$				
	25	80 115	10^{-6} cgs	sintered	2-7	Kawano et al. [A]



Lattice Parameters as a function of composition.

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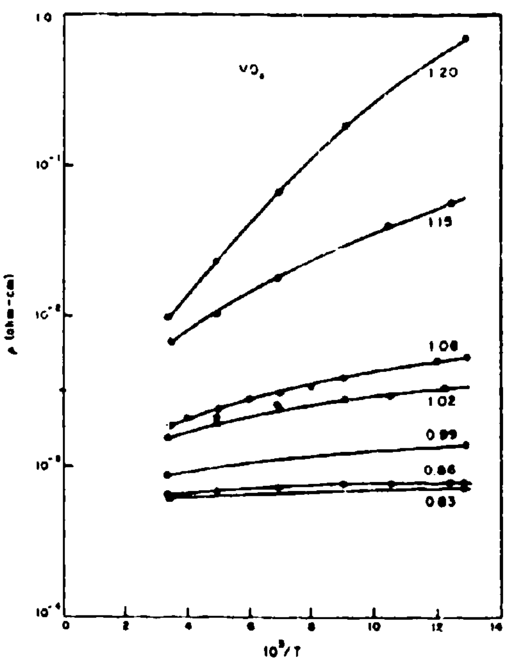
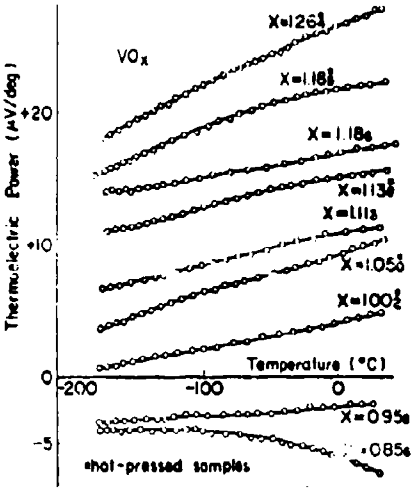
Stringer



Electrical resistivity as a function of temperature and composition for sintered samples.

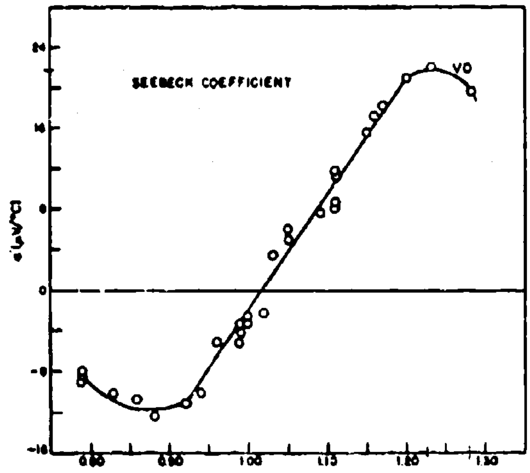
Banus et al.

$VO_{0.7-1.4}$



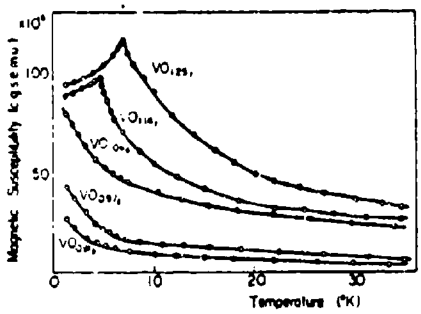
Thermoelectric power as a function of temperature for sintered VO_x

Kawano et al., B



Thermoelectric power as a function of composition in sintered VO_x

Banus et al.



Magnetic susceptibility as a function of temperature for sintered VO_x

awano et al., B

THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		VO_2				
Molecular Wgt.		82.94				
Density		4.69	g/cm^3			Donnay
Color		blue				Handbook
Symmetry		monoclinic				Donnay
Space Group		$P2_1/a$ Z-4				Donnay
Lattice Parameters	a_o	5.744	Å			Rao et al.
	b_o	4.520				
	c_o	5.376				
	β	122.6				
	V-V	2.65, 3.12	Å			Everhart & McChesney
Transition Temperature		68	°C	to rutile structure		Chamberland
Symmetry		tetragonal		(rutile)		Donnay
Lattice Parameters	a_o	4.559	Å		357	Rao et al.
	c_o	2.801				
	V-O	1.95				Bongers, Westman
	O-O	2.50, 2.87				
Temperature Coeff.	$(1/a)(da/dT)$	0.5	$10^{-5}/°K$		340-550	Bongers
	$(1/c)(dc/dT)$	3.6				
Melting Point		1818	°K			Cook, TPRC, p. 5[illegible]2
Specific Heat		0.157	cal/g °K		300	TPRC, Berglund & Guggenheim
		0.25			1700-1900	TPRC

THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE		UNIT	NOTES	TEMP. (°K)	REFERENCES
Debye Temperature		750		°K		300	Berglund & Guggenheim, Derbenwick
Thermal Conductivity		65		mW/cm °K		300-360	Berglund & Guggenheim
Thermal Expansion Coefficient		24		10^{-6} /°K	monoclinic, single crystal, ∥ c-axis	68°C	Guntersdorfer
		∥-a	⊥-a				
		26	4.9	10^{-6} /°K	tetragonal, single crystal	137°C	Hazony & Perkins, Bongers
Young's Modulus		2		10^{12} dynes/cm^2	monoclinic	300	Guntersdorfer
ELECTRICAL PROPERTIES							
Dielectric Constant		E ⊥ a	E ∥ a				
Optic	ε_∞	10.0	9.7		reflectivity meas. at 1-90μ on single monoclinic crystal	300	Barker et al.
Static	ε_o	40.6	25.9				
Optic							
Monoclinic		5.6	5.54		at 0.3-6μ	300	Verleur et al.
Monoclinic		4.26			1000 Å film at 0.25 to 4μ	300	
Tetragonal		3.95			1000 Å film at 0.25 to 6μ	355	
Optic		0.6	1.2μ				
Monoclinic		8.5	9.5		single crystals & sputtered films	300	Derbenwick
Tetragonal		6	-1			350	
Optic		E ⊥ a	E ∥ a				
Tetragonal		3.77	4.17		single crystal at 0.25 to 3μ	355	Verleur et al.

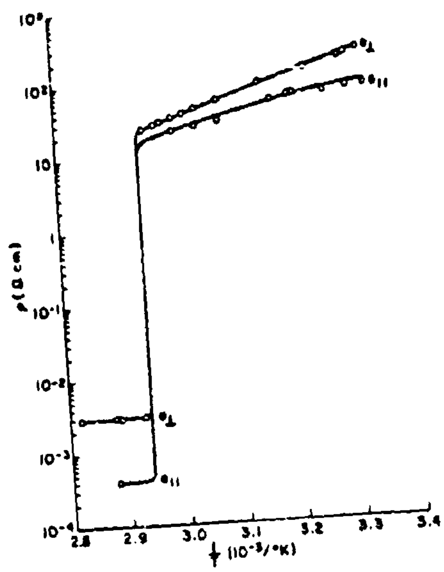
ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Dielectric Constant Pressure Coeff.	$(1/\varepsilon)(d\varepsilon/dP)$	-2	10^{-6}/bar			Neuman et al.
Resistivity		5 10^{-4}	Ω-cm	high purity, single crystal	293 341	Bongers, McChesney & Guggenheim, Bando et al., Ladd & Paul
		5×10^{3}		single crystal	4	Austin & Turner
		10^{-5} 100 25	f (Hz) 0 10^{3}-10^{8} 10^{10}	single crystal, ‖-[100]	300	Kabashima et al.
		‖c-axis	‖a-axis			
		4×10^{-2}	10^{-2} Ω-cm	epitaxial films on rutile	300	Koide & Takei
		2×10^{-3}	4×10^{-4}	monoclinic crystals	300	Everhart & McChesney
Temperature Coeff.	Ω-cm 4.2 2.3	TCR -0.036/°C -0.106/°C	Thickness 700 Å 1000	sputtered films	300	Hensler et al.
Pressure Coeff.	$d\rho/\rho dP$	-2 -3.5	10^{-5} cm^2/kg	single crystal, P= 5×10^{3} kg/cm^2	293	Ladd & Paul, Guntersdorfer, Neumann et al.

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTIES	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Transition Temperature	T_c	68°C				Chamberland
Pressure Coeff.	dT_c/dP	+8.02	10^{-5}°K/kg cm^{-2}	single crystal, P= 4×10^4 kg/cm^2 dρ= 10^4 Ω-cm		Berglund & Jayaraman
		+5.90		high purity, single crystal, P= 8×10^3 kg/cm^2		Ladd & Paul, Neumann et. al.
Transition Time		20	nsec.	1600 Å thick film, sputtered on glass		Roach & Balberg, Cope & Penn
Mobility		0.05 0.01	cm^2/V sec	sputtered film, powder	273 370	Hensler, Kitahiro et al.
		0.6 15-20		single crystal, 1 Ω-cm	300 353	Barker et al.
Effective Mass						
Electron	m_n	0.5-4	m_o	metallic state, calc. from optical and electric meas.	>68°C	Barker et al., Berglund & Guggenheim
	m_{dn} m_n	1.6-7 1-4		semiconducting state	<68°C	
	m_n	7.1 1		single crystal, sputtered films	>68°C <68°C	Hensler
Energy Gap		0.6-0.7	eV	optical meas. at 0.3-6μ on a film, electrical meas. on a single crystal, photoemission meas. on a film	<68°C	Verleur et al., Heywang & Guntersdorfer, Powell et al.

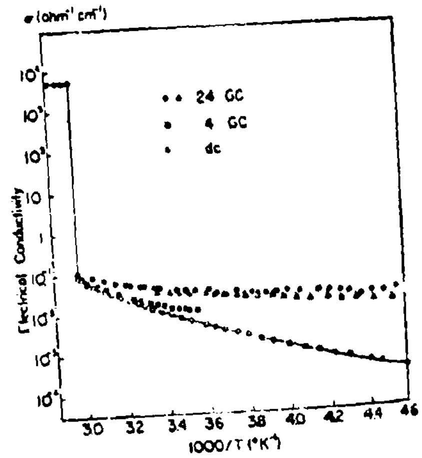
THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTIES	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Energy Gap						
Pressure Coeff.	dE_g/dP	$\sim -10^{-6}$	eV/kg cm^{-2}	semiconducting state		Berglund & Jayaraman
Deformation Potential		8	eV	piezoresistance meas. on single crystal	300	Guntersdorfer
Photoemission Threshold		5.4 4.8	eV	5μ film	298 373	Powell et al.
Quantum Yield		7×10^{-3} 2×10^{-2}	electrons/proton		298 373	Powell et al.
Seebeck Coeff.		-21.1 -23.1 -30 to -400	μV/°C	‖ c-axis ⊥ c-axis	75°C 300	Berglund & Guggenheim, Hensler
		-900 -750		single crystal	293 333	Kitahiro & Watanabe, Bongers
		-130		700-1300 Å, single crystal, sputtered films	300	Hensler
Magnetic Susceptibility	X_g	0.88	10^{-6} cgs	single crystals	100-300	Barker et al., Hill & Martin
		⊥-c ‖-c 0.85 1.0 7.9 8.4	10^{-6} cgs	single crystal	293-340 340-373	Berglund & Guggenheim
Reflectivity		metallic		λ= 0.7-0.8μ	70°C	Mokerov & Rakov, Barker et al.
Emissivity		2.5 4.4 2.0	10^{-2} W/cm^2	single crystal	300 340 341	Boyle & Verleur



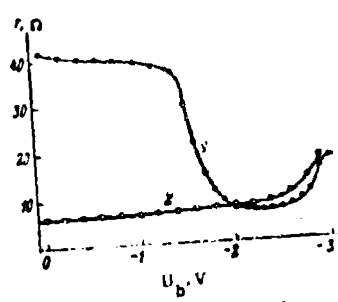
Resistivity of single crystal VO_2 as a function of temperature, measured parallel and normal to the monoclinic a-axis.

Everhart & McChesney



The dc and microwave conductivities of single crystals, as a function of temperature.

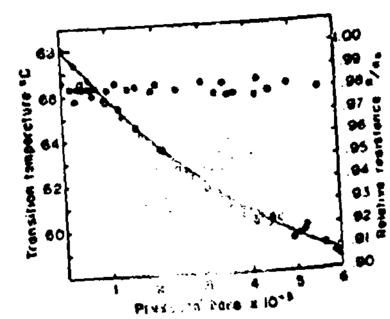
Kabashima et al.



Resistance as a function of bias voltage at 296°K.

1. Increasing voltage
2. Decreasing voltage

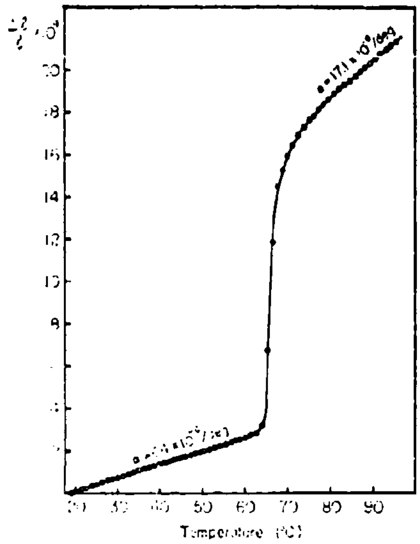
Valiev et al.



Pressure dependence of the transition temperature in single crystal VO_2 at 24.5°C

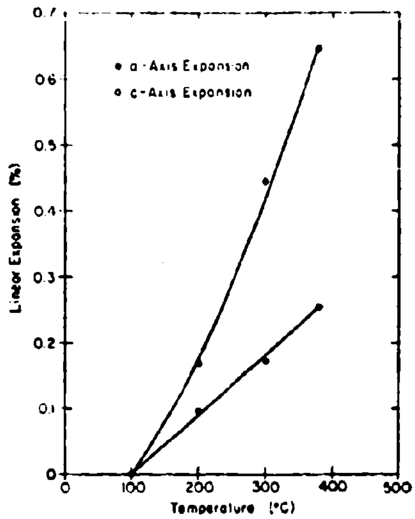
○ increasing pressure
◇ decreasing pressure
● resistance normalized to atmospheric pressure

Neumann et al.



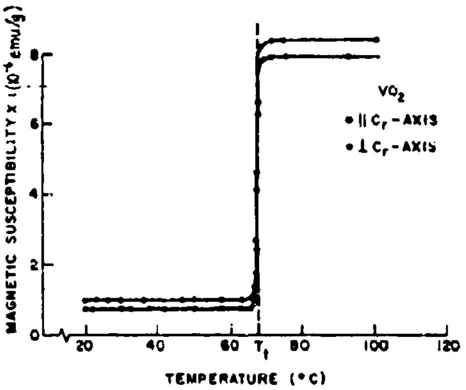
Thermal expansion as a function of temperature for sintered VO_2

Kawakubo & Nakagawa



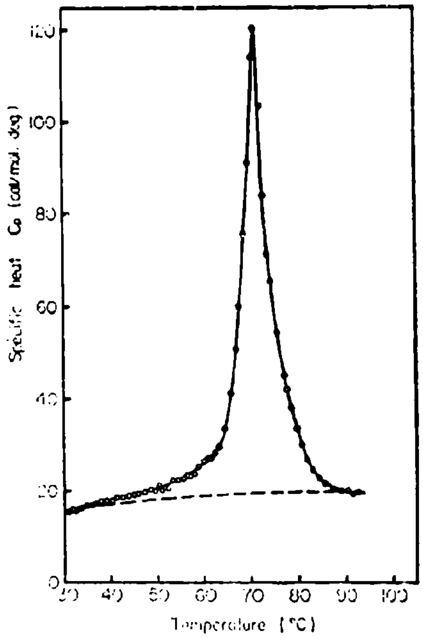
Thermal expansion of tetragonal VO_2 along two axes.

 Kirchner



Magnetic susceptibility as a function of temperature in single crystal VO_2 near the transition temperature. Measurements are parallel and normal to the rutile c-axis.

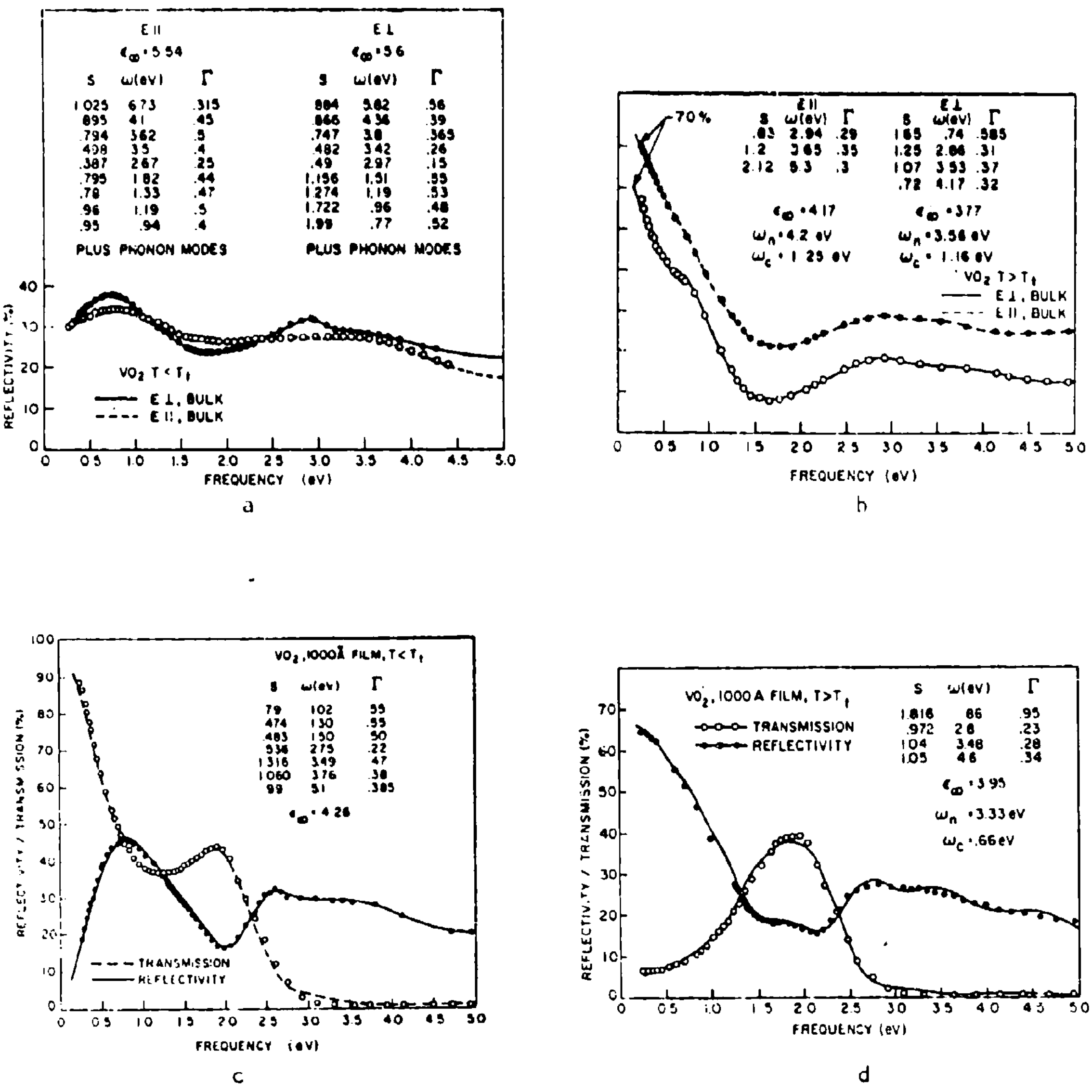
 Berglund & Guggenheim



Specific heat as a function temperature for sintered Vo..

Kawakubo & Nakagawa

VO_2 - OPTICAL PROPERTIES

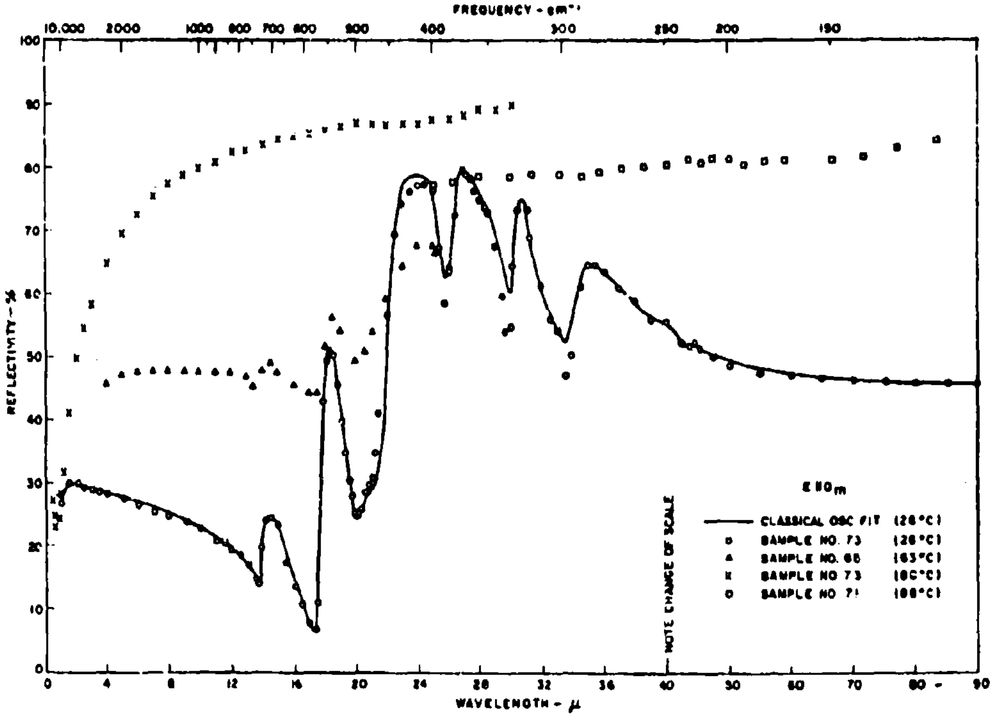


Reflectivity/Transmission data as a function of photon energy for single crystals and films of vanadium dioxide. The classical oscillator fit is shown at 300°K as well as slightly above the transition temperature, 355°K

a. bulk single crystals at 300°K
b. bulk single crystals at 355°K
c. 1000 Å film on sapphire substrate at 300°K
d. 1000 Å film on sapphire substrate at 355°K

Verleur et al.

VO_2 - REFLECTIVITY



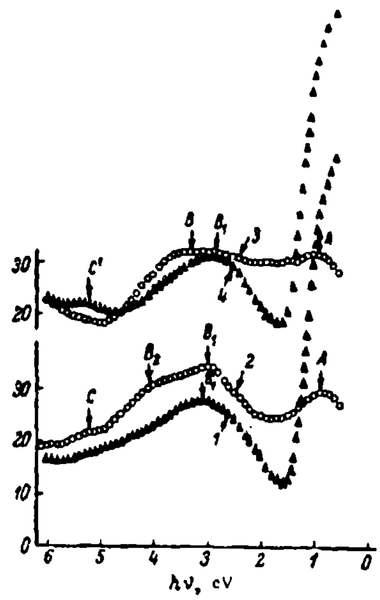
Reflectivity as a function of wavelength at three temperatures. The solid curve is a fit for data below the transition temperature, at 63°C, Data points marked by a triangle were taken on cooling.

Barker et al.

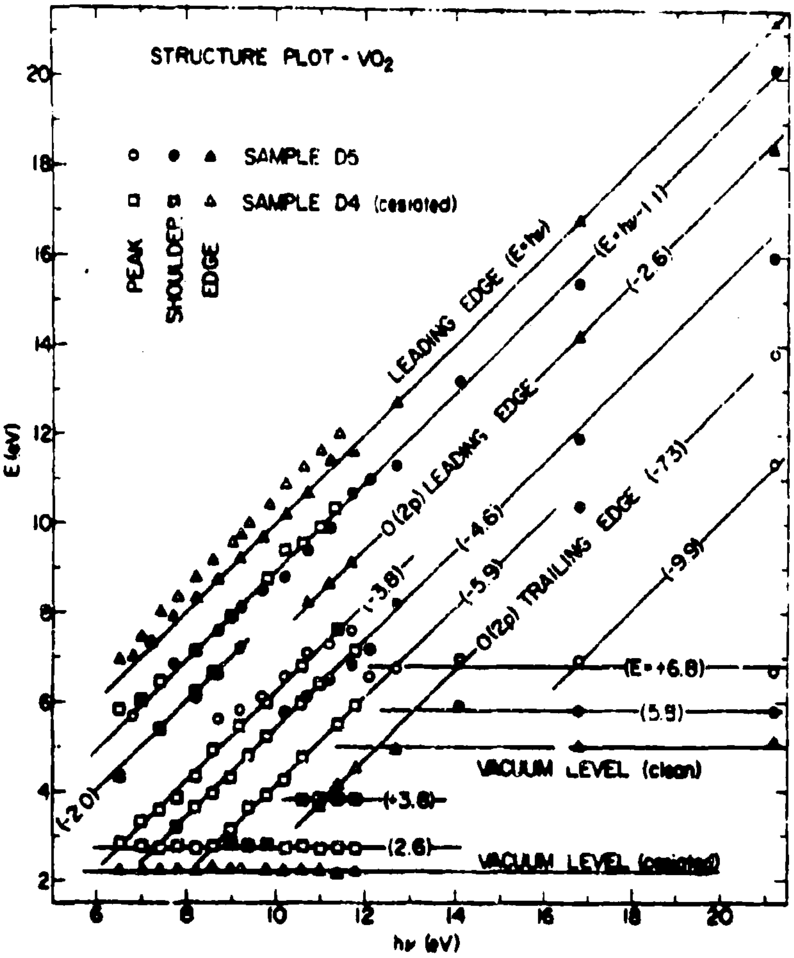
Reflectivity as a function of wavelength for single crystals, measured above and below the transition temperature.

1. E⊥ c_r above 70°C
2. E⊥ a_m at 20°C
3. E|| a_m at 20°C
4. E|| c_r above 70°C

Structure above 2 eV is associated with electron transitions; below 2 eV the reflectivity is metallic.

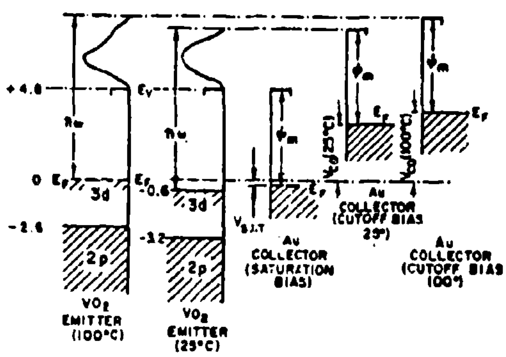


Mokerov & Rakov



Electron energy, E, is measured relative to the uppermost occupied level. The location of the structure relative to the uppermost occupied level is the same for V_2O_4 and V_4O_8 within the resolution of the photoemission.

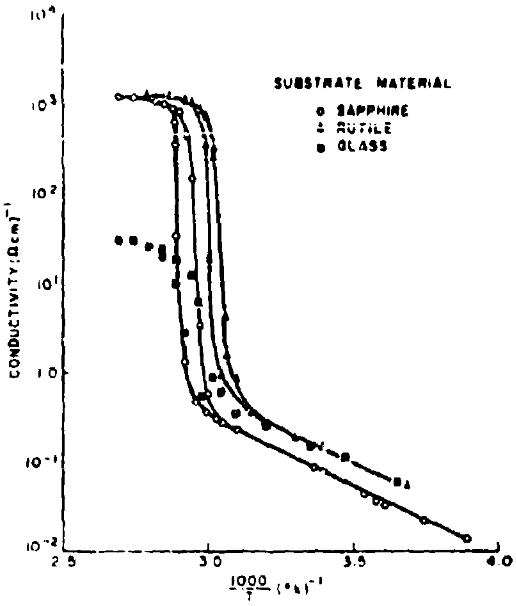
Derbenwick



Energy level and bias relationships for VO_2 above and below the transition temperature. E_f is the Fermi level and E_v marks the vacuum level. The energy zero point is placed at the Fermi level.

Powell et al.

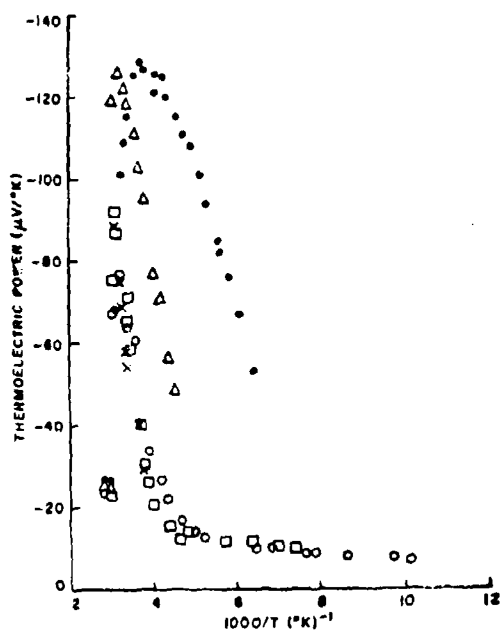
VO$_2$ - FILMS



Electrical Conductivity as a function of temperature for VO$_2$ films.

Curves show the effects of various substrates on the transition temperature.

Rozgonyi & Hensler



Thermoelectric power as a function of temperature for VO$_2$ films of varied thickness, deposited on various substrates.

×	Al$_2$O$_3$	670 Å thick
□	"	1500 Å
○	TiO$_2$	1500 Å
△	Al$_2$O$_3$	1300 Å
●	"	1300 Å

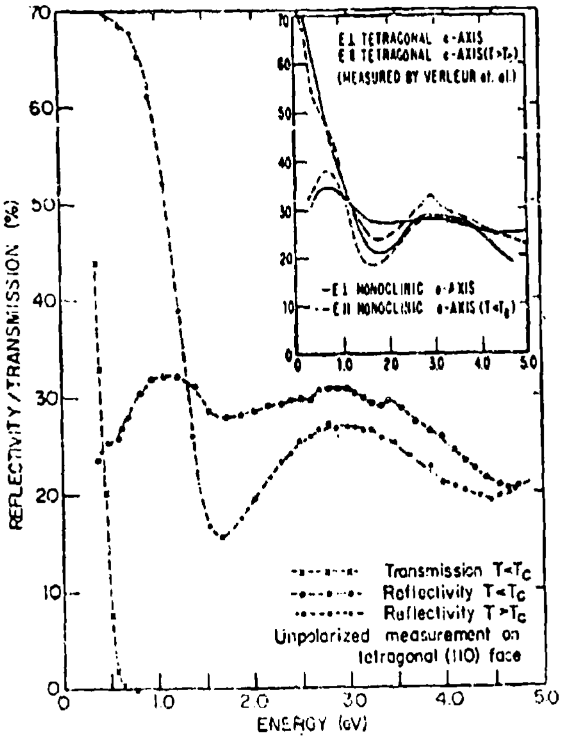
Hensler

THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V_2O_4				
Molecular Wgt.		165.884				
Density		4.4	g/cm^3			Cook
Symmetry		monoclinic			<70°C	Chamberland, Minomura & Nagasaki
Lattice Parameters	a_o	5.753	Å		335	Chamberland, Minomura & Nagasaki
	b_o	4.524				
	c_o	5.382				
	β	122.62°				
Symmetry		tetragonal		(rutile)	>70°C	Minomura & Nagasaki, King & Suber
Lattice Parameters	a_o	4.54	Å		344	Minomura & Nagasaki
	c_o	2.85				
Coefficient of Expansion		5.4	10^{-6}/°K	(tetragonal)		King & Suber
Shift in Coefficient		-1	10^{-4}/°K		67°C	Minomura & Nagasaki
Melting Point		1547	°C			TPRC, p. 532, Cook
Specific Heat		0.18 0.25 0.25	cal/g°K		300 1700 1800	TPRC, p. 532

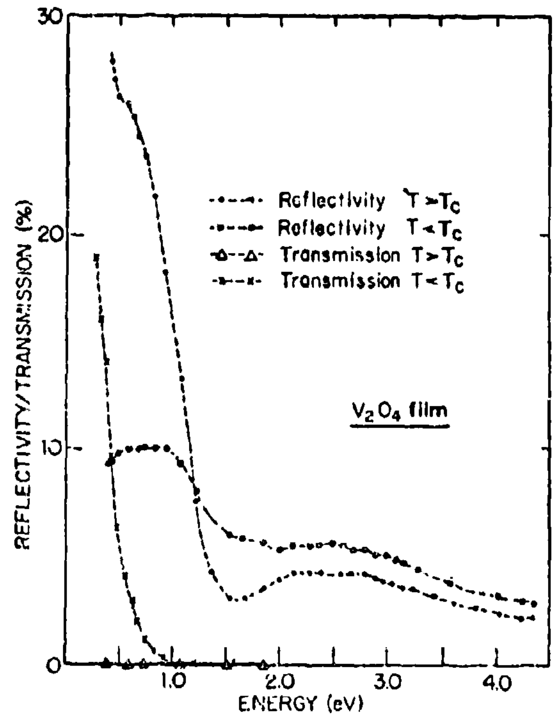
THE VAN[illegible]M-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Dielectric Constant						
Optical	ε_∞	9		tetragonal, E||c-axis	353	Barker et al.
Resistivity		10^{-4} 10	Ω-cm	single crystal, high quality, oriented ||c-axis	>339 <339	Ladd & Paul
Transition Temperature		66	°C			Ladd & Paul
Pressure Coeff.	dT_c/dP	6	10^{-5} °K/bar	P= 8 kbars		Ladd & Paul
Resistivity		10^{-2}	Ω-cm	amorphous film, rf-sputtered on substrate at 135°C	300	MacKenzie
Energy Gap	E_g	0.65	eV	transmission meas. on single crystal	300	Ladd & Paul



Reflectivity/Transmission as a function of wavelength in a single crystal, above and below the transition temperature, (300 and 360°K). Transmission is also shown for a thin sample at 300°K

Fan & Paul



Reflectivity/Transmission of a single crystal, epitaxial film, grown by vapour transport. Data are taken above (350°K) and below (300°K) the transition temperature.

Fan & Paul

THE VANADIUM-OXYGEN SYSTEM

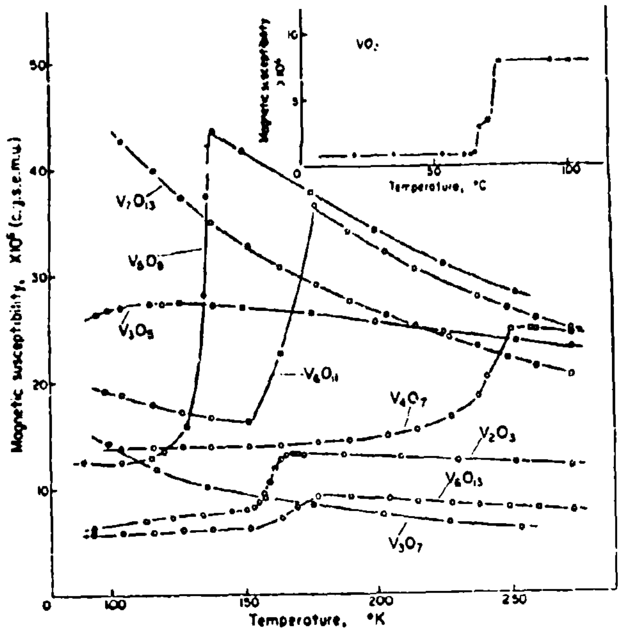
PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V_5O_9		$VO_{1.8}$		Kosuge[B]
Molecular Wgt.		398.71				
Symmetry		triclinic				Donnay
Lattice Parameters	a_o	7.004	Å			Donnay
	b_o	7.825				
	c_o	5.465				
	α	97°39'				
	β	109° 2'				
	γ	94° 6'				
Density		4.72	g/cm^3			Donnay
Electrical Resistivity		10^{-3}	Ω-cm	single crystal	130-300	Okinaka et al.[D]
		10^3-10^4			125	
Transition Temperature		130	°K	single crystal		Okinaka et al.[D]
Seebeck Coeff.		-10 to -20	μV/°K	single crystal	130-300	Okinaka et al.[D]
		-200			125	
		-800			110	
Magnetic Susceptibility	X_g	10	10^{-6} cgs	single crystal	77-140	Nagasawa et al.[A]
		45			140	Kosuge [B]
		28			265	
Néel Temperature		162	°K	sintered		Kosuge et al.[A]

THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP.(°K)	REFERENCES
Formula		V_6O_{13}		$VO_{2.16-2.17}$		Kosuge[B]
Molecular Wgt.		513.652				
Melting Point		708	°C			Kosuge[B]
Symmetry		monoclinic		$V_{12}O_{26}$		Donnay
Lattice Parameters	a_o	11.90				Donnay
	b_o	3.671				
	c_o	10.122				
	β	100°52'				
Expansion Coeff.		-1.62	10^{-4} /°K	sintered	80-173	Kosuge et al.[B]
		+1.14	10^{-5} /°K		173-300	
Electrical Resistivity		10^3	Ω-cm	sintered	300	Kachi et. al.
		$3x10^5$			156	
		$2x10^4$			157	
		$2.5x10^6$			100	
Transition Temperature		156	°K	electrical meas.		
		154		magnetic meas.		
Pressure Coeff.	dT_c/dP	-1.06	10^{-4} °K/bar	single crystal		Kosuge et al.[B]
Magnetic Susceptibility	X_g	6	10^{-6} cgs	sintered	77-150	Kosuge et al.[A,B]
		9			175	
		8			280	
Néel Temperature		155	°K			Kosuge et al.[A]

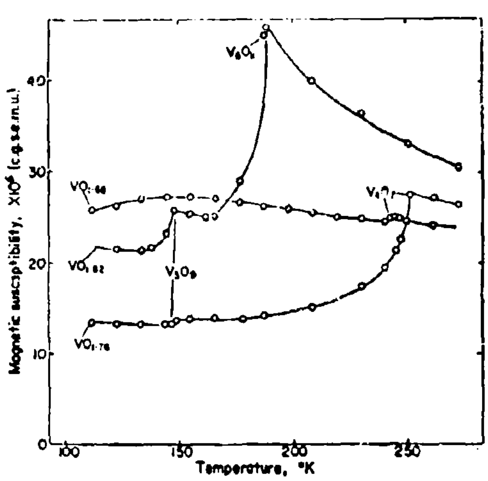
THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V_6O_{11}		$VO_{1.83}$		Kosuge[B]
Molecular Wgt.		481.652				
Electrical Resistivity		10^{-1} 10^2	Ω-cm	single crystal	177-300 177	Okinaka et al.[C]
Transition Temperature		177	°K			Okinaka et al.[C]
Seebeck Coeff.		-10 -900	μV/°K	single crystal	177-300	Okinaka et al.[C]
Magnetic Susceptibility	X_g	20 36 31	10^{-6} cgs	single crystal, T_c = 170°K	77 170 250	Nagasawa et al.[B], Kosuge[B]
Formula		V_7O_{13}		single crystal		Okinaka et al.[C]
Electrical Resistivity		10^{-3}	Ω-cm		120-300	
Seebeck Coeff.		-1	μV/°K		120-300	
Magnetic Susceptibility	X_g	44 22	10^{-6} cgs		100 250	Kosuge[B]
Formula		V_4O_7		single crystal		Okinaka et al.[E]
Electrical Resistivity		10^{-2} $2x10^{-3}$ 10^2	Ω-cm		300 250 200	
Seebeck Coeff.		-10 -230	μV/°K		250-300 200	
Transition Temperature		250	°K			
Magnetic Susceptibility	X_g	14 24	10^{-6} cgs		100-175 250-280	Kosuge[B]



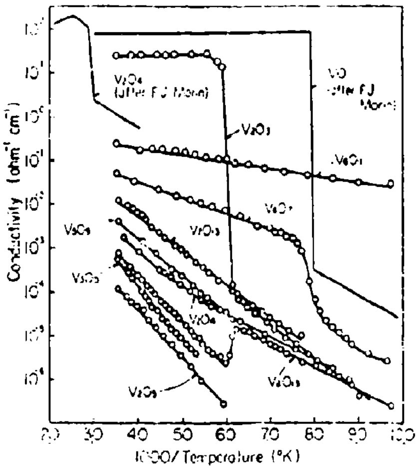
Magnetic susceptibility as a function of temperature for a series of vanadium dioxides.

Kosuge, B



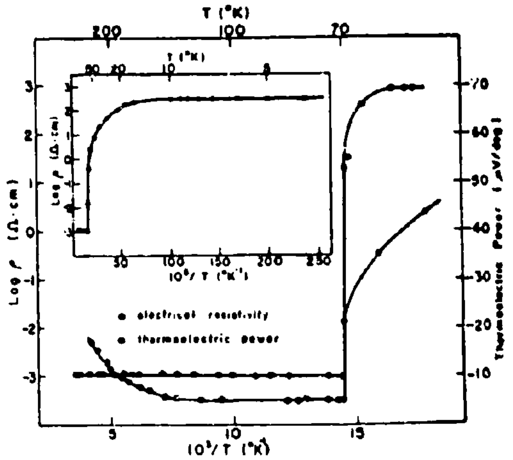
Magnetic susceptibility as a function of temperature, employed for the phase identification of a series of non-stoichiometric V_2O_4 compounds.

Kosuge, B



Electrical conductivity as a function of temperature for a series of vanadium oxides.

Kachi et al.



Electrical resistivity and thermoelectric power for V_8O_{15} as a function of temperature. The insert shows the electrical resistivity-temperature curve down to 4°K

Okinaka et al., B

THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP.(°K)	REFERENCES
Formula		V_2O_5				
Molecular Weight		181.88				
Density		3.357	g/cm^3	single crystal	298	Kennedy et al.
		2.42-2.69		amorphous		
Color		pale yellow		transparent		Kenny et al.
Cleavage		(100)		acicular habit		Donnay
Symmetry		orthorhombic				Donnay
Space Group		Pnm2 Z-2				Donnay
Lattice Parameters	a_o	11.510	Å			Bachmann et al.
	b_o	4.369				
	c_o	3.563				
Melting Point		668	°C	single crystal, loses oxygen on heating in vacuo at 600°C		Kennedy et al.
		676				Kosuge, [B] Kimizuka et al.
Specific Heat		0.167	cal/g°K		300	TPRC, p. 534
		0.227			950	
Thermal Expansion Coefficient		2	10^{-6}/°K	|| a-axis	25-600°C	Kennedy et al.
		55.4		|| b-axis		
		8		|| c-axis		
ELECTRICAL PROPERTIES						
Dielectric Constant						
Optical	ε_∞	~ 4				Kenny et al.

THE VANADIUM-OXYGEN SYSTEM

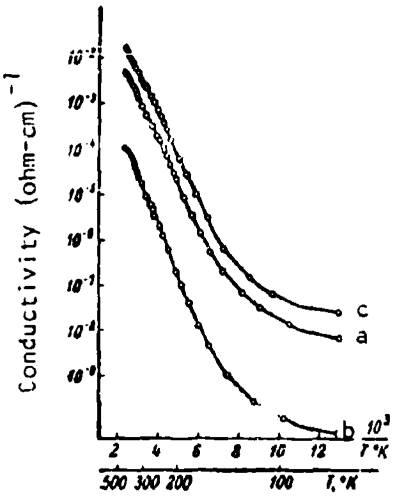
PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Dielectric Constant						
Static	ε_0	6.89		pressed powder at 6 GHz	300	Kiriashkina et al.
Resistivity	a	b	c (axes)			
	170	4700	670 ohm-cm	single crystal	298	Kennedy et al.
	5×10^8	10^{10}	2×10^8	single crystal platelets grown	100	McCulloch
	10^3	2×10^3	5×10^2	at 700°C, laminar with mirror surface	300	
	10^8	10^{10}	3×10^7	high purity, single crystal	77	Volzhenskii & Pashkovskii,
	2×10^4	10^5	200		300	Ioffe & Patrina, Patrina & Ioffe
	120	10^4	50		450	
	1.6	4	0.4 10^3 ohm-cm	single crystal	293	Allersma et al.
		25	ohm-cm	liquid in air	670°C	
		7		liquid in argon		
		10^5		high density, amorphous film	300	
		10^6		low density, amorphous film	300	
		1.1×10^6		0.5-5μ thick, amorphous film	300	Kennedy et al.
		3×10^4	ohms	P <100 kbars	300	Minomura & Drickamer
		10^3		P=100-105 kbars		
		4×10^4		P >105 kbars		
		10^4		P >300 kbars		
Mobility		5	cm^2/V sec	high purity, macrocrystalline	300	King & Suber

THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Mobility	a	b	c (axes)			
	10^{-2}	3×10^{-4}	5×10^{-2}	high purity, single crystal	300	Volzhenskii & Pashkovskii
	10^{-2}	10^{-2}	10^{-1}		440	
Energy Gap	$E_{\|\|-c}$	$E_{\|\|-a}$				
	2.34	2.36	eV	optical meas. on high purity single crystal	300	Kenny et al.
	2.49 2.30	2.54 2.32		single crystal, optical meas. at 0.47-0.56 μ	0 300	Bodo & Hevesi
Temperature Coefficient	dE_g/dT	-6.1 -7.3	10^{-4} eV/°K		293-653	Bodo & Hevesi
Seebeck Coefficient	a	b	c (axes)			
	-5.8 -9 -8.4	-6.4 -8.2 -8	-8 μV/°K -10 -9	high purity, single crystal, max. at 250°K	180 250 420	Volzhenskii & Pashkovskii
		-1000	μV/°K	single crystal	300	Ioffe & Patrina
Magnetic Susceptibility	χ_g	+0.4	10^{-6} cgs	yellow form	300	Tourky et al.
		+1.1			100-400	Roch
		H ⊥ b-axis 0.3	H || b-axis 0.2 (10^{-6})	single crystal plates, H=5 kOe	77-300	Khan et al.
OPTICAL						
Transmission		80	%	0.8 μ thick film λ = 0.52 μ		Sinclair et al.

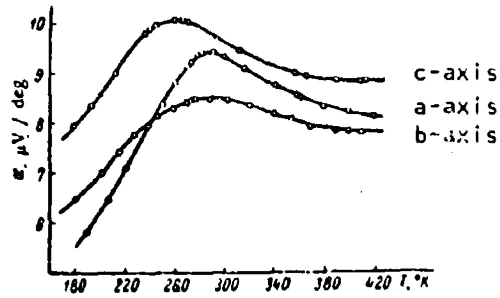
THE VANADIUM-OXYGEN SYSTEM

PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Refractive Index		Wavelength (μ)				
	0.55-0.75	0.6708	0.5893			
n_a	2.07	2.70	2.89	single crystal, birefringent	300	Kenny et al., King & Suber
n_b	1.97	2.07	2.10			
n_c	2.12	2.45	2.55			



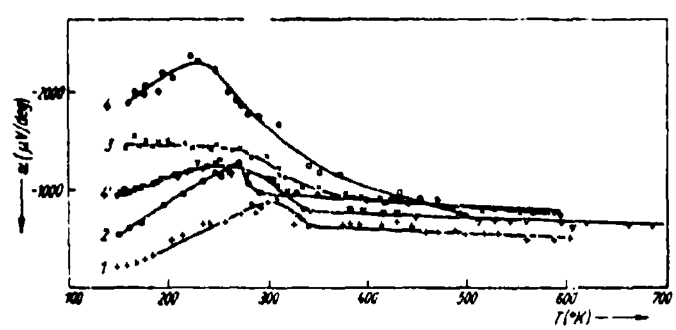
Electrical conductivity as a function of temperature in single crystal V_2O_5 along the three crystal axes.

Volzhenskii & Pashkovskii,
Ioffe & Patrina



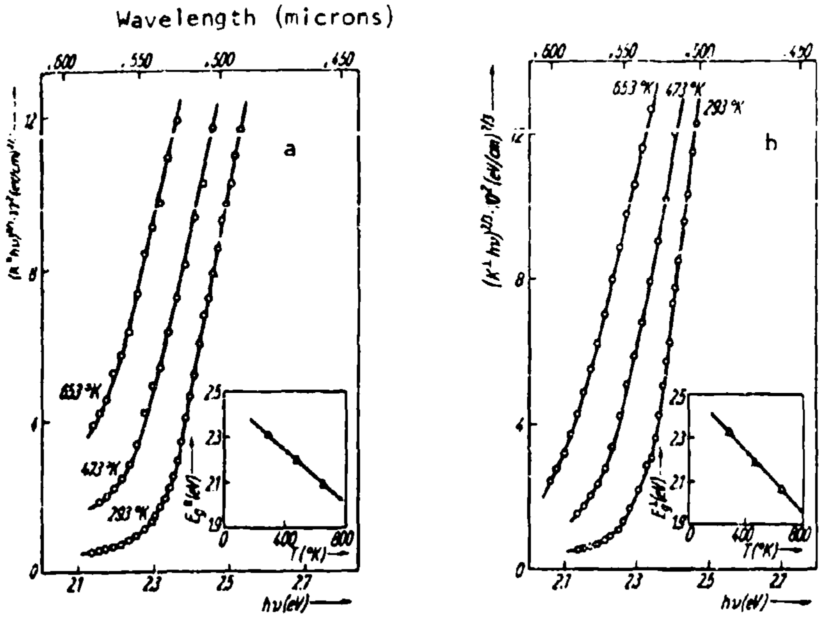
Thermoelectric power in single crystal V_2O_5 grown under 5 atm. oxygen pressure. Maximum at 250°K for thermal emf along the c-axis.

Volzhenskii & Pashkovskii



Thermoelectric power as a function of temperature for V_2O_5 single crystals. #4' is annealed at 800°K

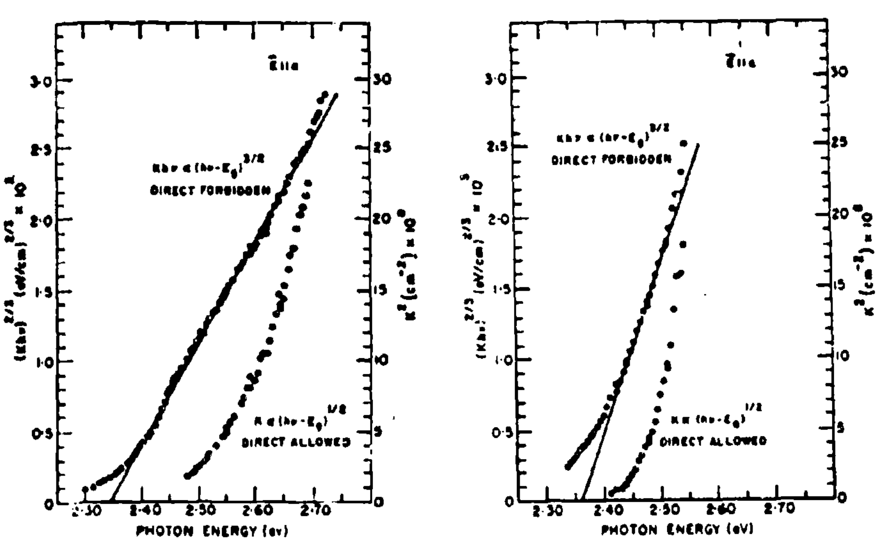
Ioffe & Patrina



Absorption edge as a function of wavelength in single crystals of V_2O_5 at three temperatures.

a. E parallel to c-axis
b. E normal to c-axis

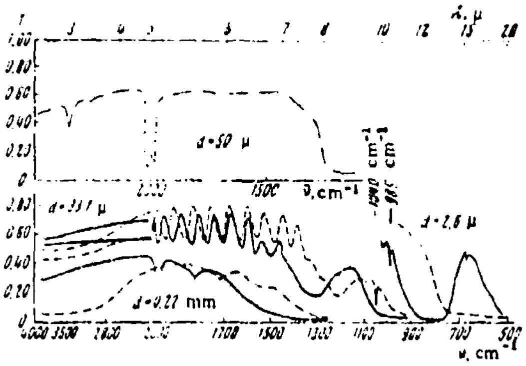
Bodo & Hevesi



Absorption edge as a function of wavelength in single crystals of V_2O_5 at 293°K.

Kenny et al.

V_2O_5 - OPTICAL PROPERTIES

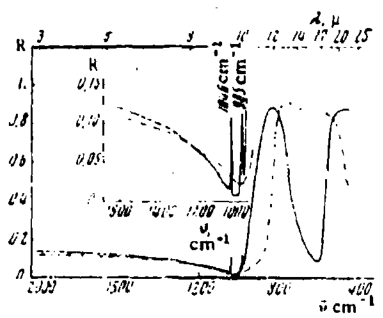


Transmission spectra of single crystals at 300°K.

------ E ‖ a

—·—·—·— E ‖ b

______ E ‖ c

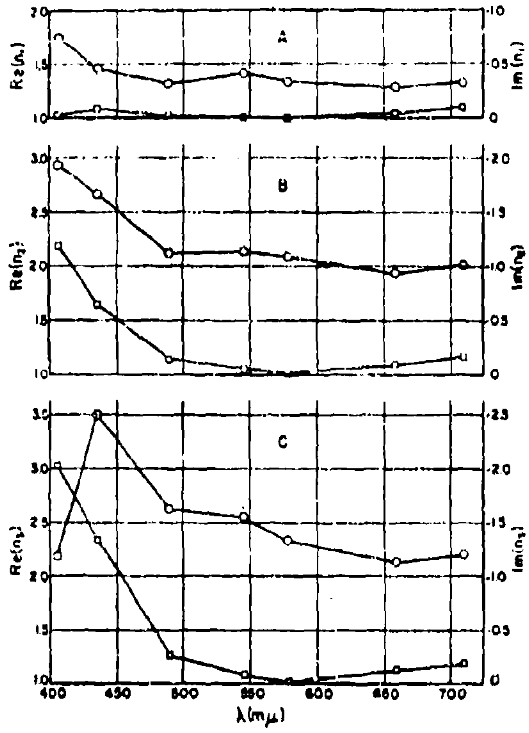


Reflectance spectra of single crystals; spectra in the narrow band region are shown in the insert.

———— E ‖ a

----------- E ‖ c

Hevesi et al.



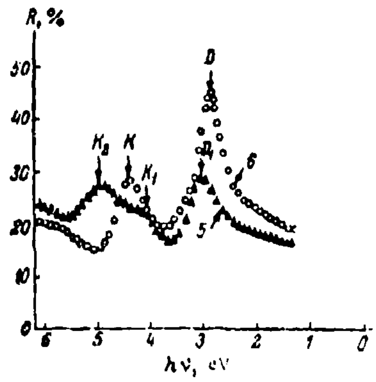
Optical constants of single crystal V_2O_5 at 300°K (monoclinic phase)

o The three refractive indices as a function of wavelength

□ Imaginary components

 Jacobsen & Kerker

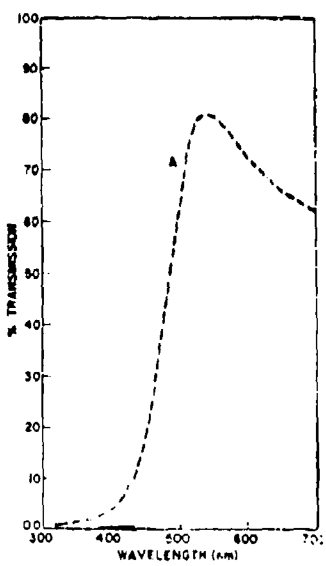
Journal of the Optical Society of America



Reflectivity as a function of wavelength for single crystals at 300°K

5. E‖c-axis, 6. E‖a-axis

 Mokerov & Rakov American Institute of Physics



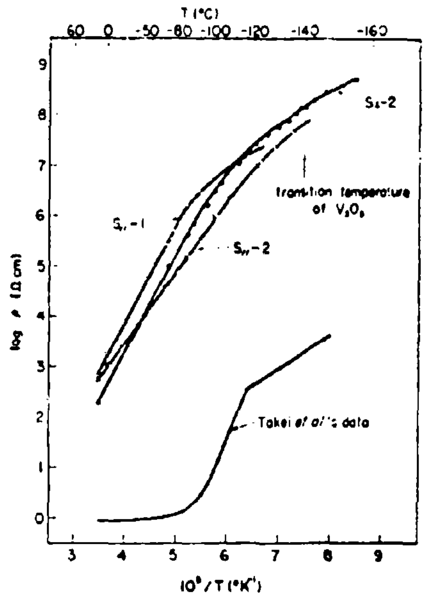
Transmission as a function of wavelength for a sputtered V_2O_5 film, 0.8 μ thick.

 Sinclair et al. Electrochemical Society

THE VANADIUM-OXYGEN SYSTEM

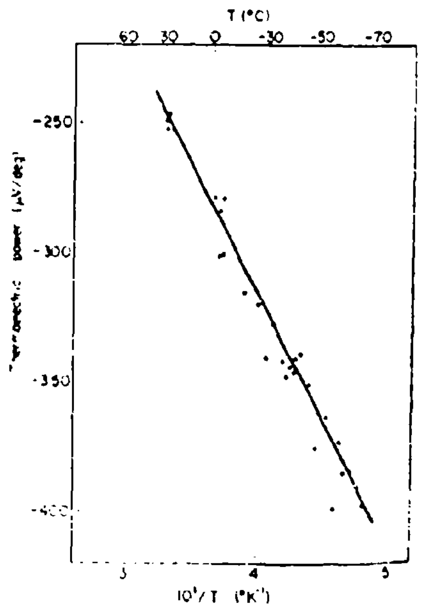
PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Formula		V_3O_5		$VO_{1.65-1.67}$		Kosuge [B]
Molecular Weight		232.826				
Density		4.55	g/cm^3			Donnay
Symmetry		monoclinic		Z-4		Donnay
Lattice Parameters	a_o	9.835	Å			Donnay
	b_o	5.031				
	c_o	6.974				
	β	109° 28'				
Electrical Resistivity		250	ohm-cm	single crystal, meas. ⊥ growth-axis, slightly anisotropic, no transition	300	Okinaka [A] et al.
		10^6			185	
		2×10^8			115	
		2×10^3		sintered	300	Kachi et al.
		2×10^5			185	
Seebeck Coefficient		-250	μV/°K	single crystals	300	Okinaka [A] et al.
		-400			200	
Magnetic Susceptibility	χ_g	24	10^{-6} cgs	single crystals	250	Nagasawa [B] et al.
		30			77	

V_3O_5 - ELECTRICAL PROPERTIES



Electrical resistivity as a function of temperature for single crystal V_3O_5 Two samples were measured; from 250 to 300°K by a four point method and below 250°K by a two point method. Measurements were made as indicated, parallel and normal to the growth axis.

Okinaka et al.



Thermoelectric power as a function of temperature for single crystals.

Okinaka et al.

THE VANADIUM-OXYGEN SYSTEM

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP.(°K)	REFERENCES
Formula		V_2O_3				
Molecular Wgt.		149.88				
Density		5.05	g/cm^3	monoclinic		Donnay
Color		black				Handbook
Symmetry		monoclinic				Donnay
Lattice Parameters	a_o	13.88	Å	<160°K		Donnay
	b_o	4.98				
	c_o	8.57				
	β	91°36'				
	V-V	2.745	Å	face (a-c plane)		Dernier & Marezio
	V-V	2.987		edge		
Symmetry		hexagonal		α-corundum		Donnay
Lattice Parameters	a_o	4.948	Å			McWhan & Rice, Nakahira et al, Newnham & de Haan
	c_o	13.97				
	V-V	2.700		face		Dernier & Marezio
	V-V	2.872		edge		
Density		4.98	g/cm^3	single crystal		Zhuze et al.[A]
Melting Point		2050	°C			Stringer
Specific Heat		0.165	cal/gr °K		300	TPRC, p. 530
		0.24			1700	
		0.25			1800	

PHYSICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Thermal Expansion		$\sim$2	10^{-4} /°K	hot pressed at 1100°C	173°C	Foëx
		$\sim$1	10^{-5} /°K		300-800°C	
ELECTRICAL PROPERTY						
Dielectric Constant						
Static	ε_o	15(±20%)		polycrystalline at 1 MHz	53	MacMillan, p. 18
		18		$V_2O_{3.7}$ pressed powder,	<160	Samokhavalov
		36		ρ_{300} = 50 Ω-cm at 10 GHz		
Optical	ε_∞	$\sim$5		single crystal	>T_c	Zhuze et al.[B]
Electrical Resistivity		1.3×10^{-4}	Ω-cm	high purity, single crystal	300-170	Goodman
		10^5			168	
		10^7			115	
	‖-c plane	⊥‖-a plane				
	3×10^{-4}	1×10^{-4}		single crystal	285	MacMillan
	5.6×10^{-4}	6.3×10^{-4}		single crystal	273	Feinleib & Paul
		10^4			150	
		10^5			120	
		12×10^{-4}			500	
		21			600	
		26			700	
		29			800	
		10^4		amorphous, sputtered film	<170	MacKenzie
		10^{-2}			>170	

THE VANADIUM-OXYGEN SYSTEM

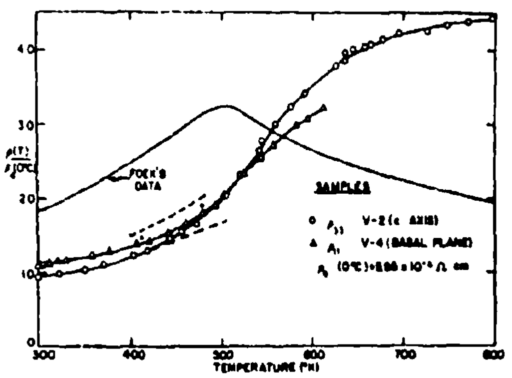
ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Electrical Resistivity						
Temperature Coeff.	$\rho(T)/\rho(0°C)$	$0.36+2.3\times10^{-3}$ T(°K)		single crystal	150-350	Feinleib & Paul
		‖-c ‖-a				
Pressure Coeff.	$d\rho/dP$	-4.3 -8.8	10^{-6} Ω-cm/kbar	P=6 kbar	300	
		‖-a				
Volume Coeff.	$(1/\rho)(d\rho V/dV)$	42 20		P=1 bar P=25 kbar	300	McWhan & Rice
Transition Temperature	T_c	172±4	°K	high purity, single crystal		Goodman, McWhan & Rice, Morin
Pressure Coeff.	dT_c/dP	-4.1	°K/kbar	P=15 kbar, single crystal	150	Austin
		-3.78		P=6 kbar		Feinleib & Paul
		-3.1		P=160 kbar	77-500	Minomura & Nagasaki
		a b c (axes)				
Stress Coeff.	dT_c/dS	-6.8 -4.1 -0.5	°K/kbar	single crystal	300	Feinleib & Paul
Mobility						
Hole	μ_p	0.55 0.40	cm^2/V sec	single crystal	200 300	Zhuze et al.[A]
Temperature Coeff.		$T^{-0.7}$				
Hole	μ_p	0.6 0.2			300 700	Austin & Turner
Hole	μ_p	1.5×10^{-4}		single crystal	125	MacMillan

THE VANADIUM-OXYGEN SYSTEM

ELECTRICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
Effective Mass	m^*	45-50	m_o	single crystal	$>T_c$	Feinleib & Paul, Adler & Feinleib
		11		optical meas. on single crystal	$>T_c$	Zhuze et al. [8]
Mean Free Path		2	Å			Feinleib & Paul, Adler & Feinleib
Energy Gap		0.1	eV	optical meas.	77	Feinleib & Paul, Adler & Feinleib,
		0.12-0.18		electrical meas.	150-170	Barker & Remeika
Pressure Coeff.	dE_{g_o}/dP	-4.4	10^{-6} eV/bar	single crystal		Feinleib & Paul, Austin
Seebeck Coeff.	$Q_{\parallel}$	10.5	μV/°K	single crystal	285	MacMillan
	$Q_{\perp}$	3.2				
	Q	+350 -400		p-type n-type	100 100	
	$Q_{\parallel}$	~12 <-5			170-500 100-150	Austin & Turner
Magnetic Susceptibility	χ_g	$\sim 10^{-7}$	cgs	single crystal	>170	MacMillan
		3.8 6.4	10^{-6} cgs	pressed powder	90 293	Bogdanova & Loginov
		$\chi_{\parallel}$ $\chi_{\perp}$ 6.9 5.9 11.2 12.2	10^{-6} cgs	single crystal	<170 >170	Carr & Foner, Nakahira et al.
		12.42 12.56 11.24 10.88		single crystal	300	Arnold & Mires, Gossard & Menth

THE VANADIUM-OXYGEN SYSTEM

OPTICAL PROPERTY	SYMBOL	VALUE	UNIT	NOTES	TEMP. (°K)	REFERENCES
			Wavelength (μ)			
Transmission		0	0.2-20		300	Feinleib & Paul, Barker & Remeika
		maximum	6		77	
Refractive Index		1.84	0.4	single crystal	300	Zhuze et al. [B]
		1.67	1.0			
		1.95	2.0			
		6.8	10.0			
		8.8	20.0			



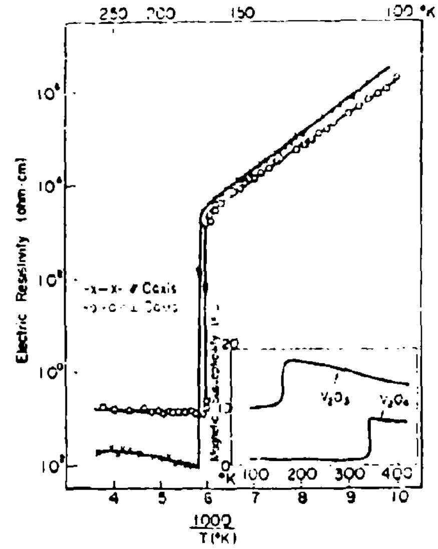
Electrical resistivity as a function of temperature to 800°K for single crystals.

ρ_{33} measured along c-axis

ρ_{11} measured in basal plane

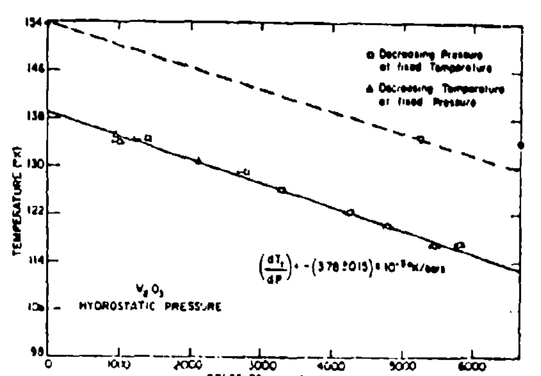
Foex's data on sintered bars are included.

Feinleib & Paul



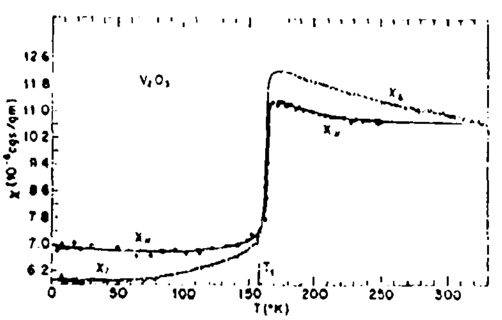
Resistivity as a function of temperature in single crystals.

Kosuge, A



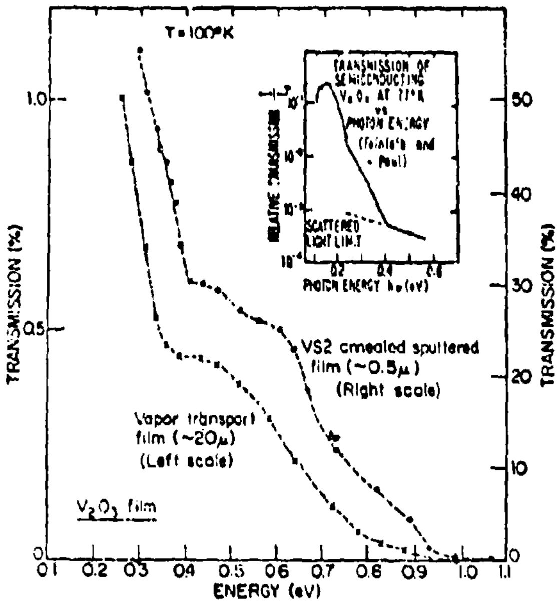
Transition temperatures as a function of hydrostatic pressure in single crystals.

Feinleib & Paul



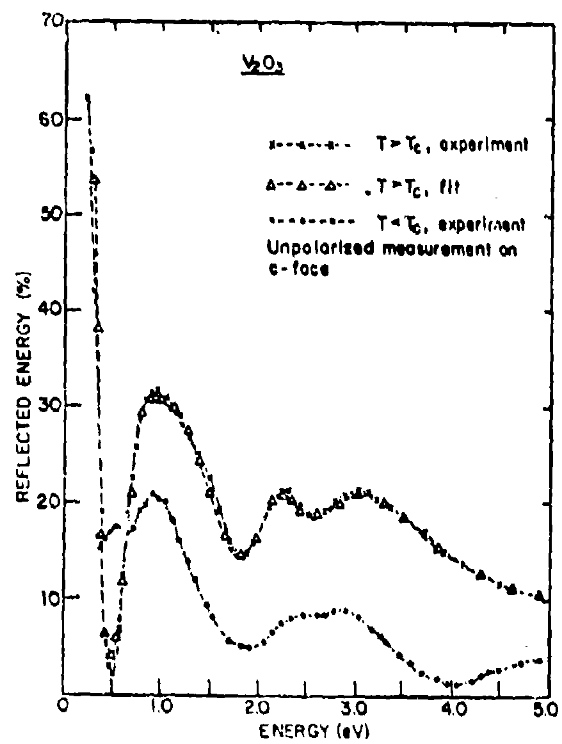
Magnetic susceptibility as a function of temperature in single crystals, parallel and normal to the basal plane.

Carr & Foner



Low temperature transmission of a single crystal, epitaxial V_2O_3 film grown by vapour transport and of an annealed, sputtered film. Data from these two films are compared with transmission from a single crystal as reported by Feinleib and Paul.

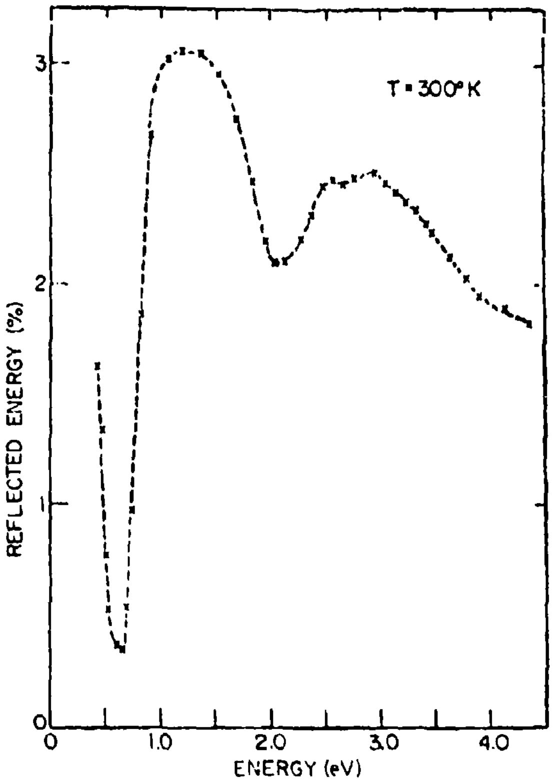
Fan & Paul



Reflectivity of a single V_2O_3 crystal, above and below the transition temperature.

Fan & Paul

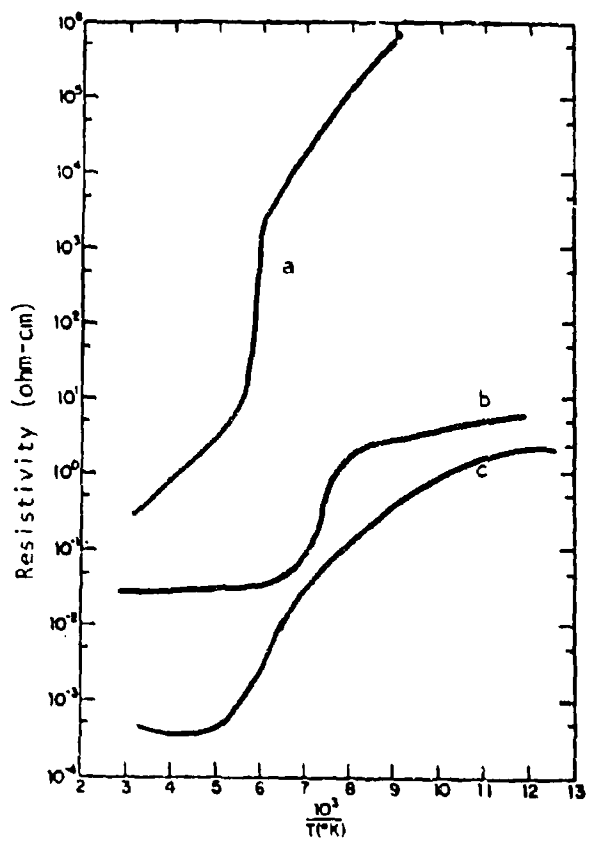
V_2O_3 - FILMS



Reflectivity as a function of wavelength for a single crystal, epitaxial film. The substrate is single crystal alumina with the c-axis normal or parallel to the substrate plane.
T_1 = 800°C, T_2 = 60°C

Measurements in the infrared and visible are made above the transition temperature.

Fan & Paul



Electrical resistivity as a function of temperature for V_2O_3 films.

a. sputtered, polycrystalline film, about 0.55μ thick, alumina substrate, annealed at 600°C
c. similar film but showing great difference in resistivity

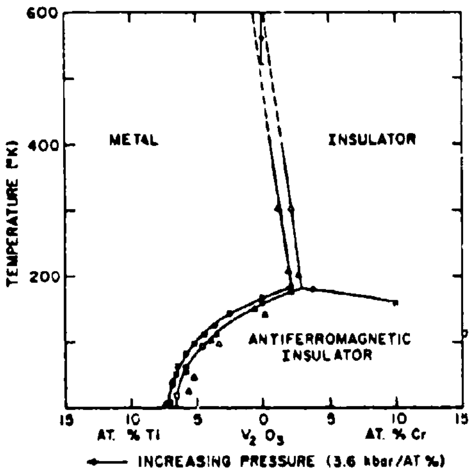
b. single crystal, epitaxial film, grown by vapour transport on alumina substrate

Fan & Paul

Crystal Structure, Transition Temperature and Conductivity in $V_{1-x}Ti_xO_2$

Composition	Monoclinic (25°C)				Rutile		Transition Temp. (°C)	Conductivity at 40°C $(ohm\text{-}cm)^{-1}$
x	a_o	b_o	c_o	β	a_o	c_o		
0.00	5.744	4.520	5.376	122.6	4.559	2.801	69	0.8
0.02	5.729	4.530	5.364	122.3	-	-	65	1.2
0.05	5.727	4.560	5.390	122.5	4.545	2.844	63	-
0.10	5.716	4.499	5.424	122.0	4.537	2.868	60	5.8
0.20	5.704	4.490	5.448	121.3	4.539	2.891	58	4.7
0.40	4.833	4.380	5.530	97.9	4.546	2.894	48	0.3

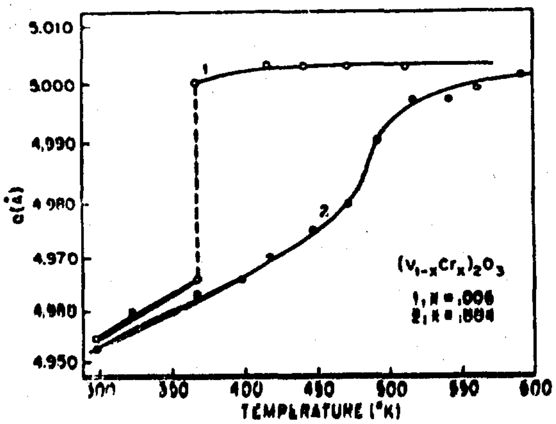
Rao et al.



Generalized phase diagram of transition temperature as a function of both pressure and at. % of chromium and titanium in V_2O_3

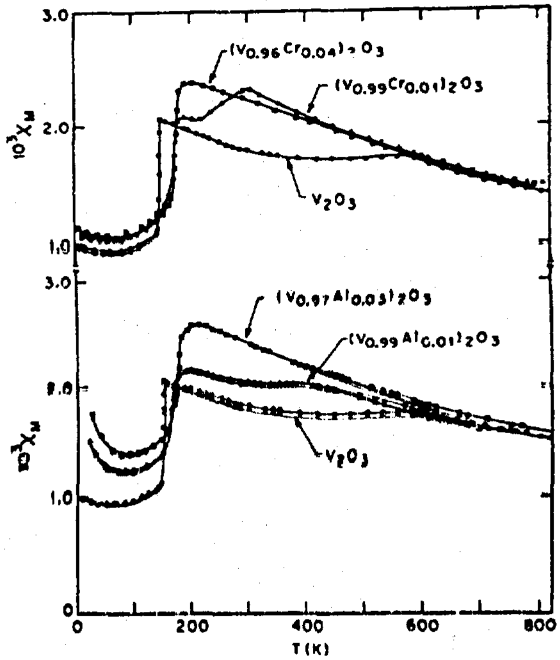
- ● mixed oxides at 1 atm.
- ■ ▢ V_2O_3 on increasing and decreasing pressures, resp.
- ▲ △ $(V_{0.96}Cr_{0.04})_2O_3$ for increasing and decreasing pressure

 McWhan et al.



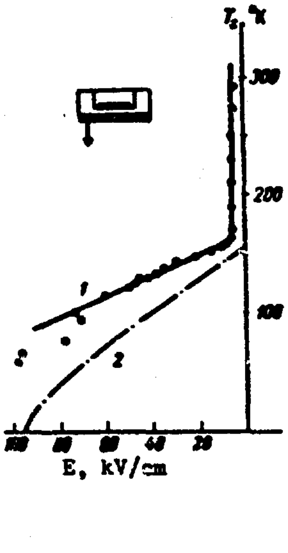
Lattice parameters as a function of temperature for two chromium-doped V_2O_3 crystals.

Jayaraman et al.



Magnetic susceptibility as a function of temperature for V_2O_3 and for chromium and aluminum containing V_2O_3. The undoped and chromium containing V_2O_3 were single crystals and the susceptibility was measured parallel to the c-axis. The aluminum containing samples are ceramic powder aggregates.

Gossard et al.



Transition temperature as a function of electrical field in sintered $(V_{0.91}Cr_{0.09})_2O_3$. The electrical field shifts the transition temperature similarly to the shift by hydrostatic pressure.

Andreev et al.

INITIAL RATE OF CHANGE OF UPPER TRANSITION TEMPERATURE WITH COMPOSITION (dT_t/dx) FOR THE SUBSTITUTIONAL COMPOUNDS

$$V_{1-x}M_xO_2$$

[Critical compositions x_1 and x_2 indicate phase changes at 300°K. Room-temperature structures within the regions $x_1<x<x_2$ and $x>x_2$ are also indicated, where mono. refers to the monoclinic (P2/c) phase and ortho. to the orthorhombic (probable space group F222) phase.]

M	dT_t/dx (°K/at % M)	x_1	x_2	$x_1 < x < x_2$	$x > x_2$
Cr^{3+}	~+3	0.01	0.20	ortho.	$(2\phi)^*$
Fe^{3+}	+3	0.01	0.125	ortho.	two-phase
Ga^{3+}	+6.5	0.005	0.02	ortho.	two-phase
Al^{3+}	+9.0	0.005	0.045	ortho.	two-phase
Ti^{4+}	−0.5 to −0.7	0.2	0.2 to 0.25	ortho.	rutile and $(2\phi)^*$
Re^{4+}	~−4	0.07		rutile	
Ir^{4+}	~−4	0.04	0.5	rutile	two-phase
Os^{4+}	−7	0.03	0.1	rutile	two-phase
Ru^{4+}	−10	0.025	0.75	rutile	two-phase
Ge^{4+}	+5				
Nb^{5+}	−7.8	0.05	0.9	rutile	NbO_2
Ta^{5+}	−5 to −10	0.02	0.5	rutile	two-phase
Mo^{6+}	−5 to −10	0.03	0.55	rutile x = 1.0	$(2\phi)^*$ mono.
W^{6+}	−28	0.013	0.68	rutile	ortho.
ordered trirutile phase about x = 0.33; 0.78 < x < 0.8 $(2\phi')^*$ phase; 0.85 < x < 1 mono.					

* The 2ϕ phase is a distorted rutile structure with orthorhombic symmetry, and the $2\phi'$ phase is similar but with monoclinic symmetry.

Goodenough and Pierce

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